Artificial superlattices grown by MBE: could we design novel superconductors?

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Abstract - We review briefly the technique of Atomic-Layer-by-Layer Molecular Beam Epitaxy (ALL-MBE) that allows us to deposit atomically smooth single-crystal thin films of cuprate superconductors and various other complex oxides. We give a couple of examples showing how this technique has been used to synthesize 'artificial' high-T_c superconductors - metastable high-n members of known cuprate families or superlattices of various known (natural, stable) compounds. We also report briefly on the present status of our state-of-the-art ALL-MBE system, and suggest that this technique could be useful in search for new natural or artificial superconducting materials.

Keywords: Molecular beam epitaxy, high-temperature superconductivity, complex oxides, artificial superlattices.

I. Introduction: Layered superconductors

Discovery of high-temperature superconductivity in cuprates in 1986 [1] greatly increased interest in layered superconductors. Indeed, it has been well established that the new high-T_c cuprates are native superlattices, where metallic CuO_2 layers are stacked in alternation with nonmetallic oxide layers, for instance $(La,Sr)_2O_2$ layers in $La_{2-x}Sr_xCuO_4$ (LSCO), $Bi_2Sr_2O_4$ layers in $Bi_2Sr_2CuO_6$ (Bi-2201), and Y and BaO layers in $YBa_2Cu_3O_7$ (YBCO). Experimental evidence in support of this picture includes the demonstration that T_c stays constant even if individual high-T_c (Bi-2212) layers [2,3], observation of intrinsic Josephson effects in BSCCO [4], LSCO [5], and YBCO [6], etc.

Is this layered crystal structure a critical prerequisite of high temperature superconductivity? We do not know for sure, since the mechanism of HTS is still controversial; we also do not know what the maximum T_c in materials of this type might be. On the optimistic side, V.L. Ginzburg proposed already 40 years ago [7] that high-temperature superconductivity could occur via exciton-mediated electron pairing, in superlattices made by alternating thin metallic and dielectric layers (see Fig. 1). However, to the best of our knowledge, no one has tried to realize this idea experimentally. Perhaps this neglect can be attributed to obvious and substantial technical difficulties - it was clear that one would need to control the thickness and the stoichiometry of alternating layers with extreme accuracy. Fortunately, in the last decade significant technological advances have been made and today this ambitious task is fully within reach, as we detail next.

II. Atomic-Layer-by-Layer Molecular Beam Epitaxy (ALL-MBE)

Molecular beam epitaxy (MBE) is an ultra-high vacuum technique for deposition of thin films, usually from resistively-heated thermal evaporation sources (also known as thermal effusion cells or Knudsen cells). Electron-beam sources can be employed as well, in particular for refractory metals, but in this case the atomic fluxes may be somewhat less stable. MBE sources can be shuttered, and if the system is equipped with some monitoring tools that allow for an accurate control of absolute deposition rates of respective metals, one may achieve Atomic-Layer-by-Layer (ALL) growth. Notice that the deposition process must be controlled very accurately – at the level of one percent of an atomic monolayer, or better.

Our ALL-MBE system (see Fig. 2) is equipped with 16 metal sources (either K-cells or rod-fed electron-beam sources), a distilled ozone source, and a sophisticated, real-time, 16-channel rate monitoring system based on atomic absorption spectroscopy. It is also provided with reflection high-energy electron diffraction (RHEED) system with sample scanning capability and a unique time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) system for real-time chemical analysis of the film surface. These advanced surface-science tools provide real time information about the film surface morphology, chemical composition, and crystal structure, and are quintessential for the success in

growing atomically smooth and perfect films. The system is completely modular, and it is possible to recharge or replace a source element within minutes, even during film growth. The controlling software allows us to track the temperature of all the sources, the ozone pressure, the substrate position and orientation, the deposition rates from each of the sources, etc., and to control or modify the stoichiometry within each monolayer. This provides great flexibility in depositing different HTS compounds and other oxides. In particular, the machine is well suited, by design, for depositing alternating layers with the precision better than a single atomic layer, and hence for synthesis of artificial superlattices. More details about the system have been reported elsewhere [8]. The machine we actually built at Oxxel GmbH in Bremen, Germany, and it has been acquired subsequently by Brookhaven National Laboratory where it is placed now. The system is fully functional and HTS films are being deposited daily. At the time of writing of this report, we have already performed over 460 growth experiments.

III. Atomic-layer engineering of complex oxides by MBE: some results so far

ALL-MBE enables material engineering at various levels. By stacking of molecular layers of different compounds, one can form various multilayers. Within a molecular layer, one can add or omit atomic monolayers and thus cast novel compounds.

In this section we review briefly some of our 'classic' results and also some more recent experimental findings that illustrate the capability of ALL-MBE. Already well over a decade ago, the Varian group (J. Eckstein and I. Bozovic) achieved T_c = 20 K in Bi-2201, and T_c = 90 K and j_c(T=4.2K) = 2.5x10^7 A/cm^2 in Bi-2212 films, as-grown. Structural perfection of layers and interfaces on an atomic scale had been demonstrated by RHEED, SEM, atomic force microscopy (AFM), and subsequently also by planar and cross-section transmission electron microscopy (TEM) [9]. The cross-section TEM image in Fig. 3 shows essentially perfect Bi-2201 / Bi-2212 interfaces. This technical advance enabled synthesis of precise $[(Bi-2201)_n + Bi-2212]_m$ superlattices, with n = 1, 2, …, 10. In-plane transport measurements showed that the superconducting transitions in such superlattices are essentially identical to those in thick single-phase Bi-2212 films. [2] Specifically, there was no significant decrease of T_c as the number of the spacer Bi-2201 lay-

ers inserted between single-slab Bi-2212 layers was increased, see Figure 4. The fact that the same T_c was observed indicated that Bi-2212 layers were well connected (in-plane) on a macroscopic length scale, even though they were only one-half unit cell (15.4 Å) thick. More importantly, the same experimental observation demonstrated unambiguously that HTS phenomenon is essentially quasi-2D in nature. In Bi-2212, the HTS layers are only weakly (Josephson) coupled along the c-axis. This conclusion found a spectacular confirmation in subsequent observation of Josephson effects such as emission of electromagnetic radiation from a Bi-2212 single crystal biased with a dc voltage. [4-6] More recently, we have also seen undiminished T_c in superlattices with a single unit cell thick LSCO layers spaced away by thicker, undoped, insulating LCO layers. [10]

A major advantage of the ALL-MBE method of film deposition is that it allows for precise control of layering, which in turn makes possible growth of BiSrCaCuO phases that do not exist as bulk equilibrium compounds. For example, ALL-MBE has been used to grow films of metastable Bi-2234, Bi-2245, and Bi-2278 phases. These films were superconducting; the highest T_c observed in a single-phase Bi-2278 films was 60 K. At BNL, we have recently observed $T_c = 75$ K in a Bi-2201: Bi-2234 superlattice. Note that few other groups have grown these higher-n members of the $Bi_2Sr_2Ca_{n-1}Cu_nO2_{n+4}$ family as well, even though they used somewhat simpler thin-film deposition techniques such as sputtering or laser ablation. However, in these cases there was no detailed (atomic layer) control of the kinetics of arrivals of metal atoms on the growing film surface, and hence such films typically contained many stacking faults and intergrowths of various n-members. Given what we have demonstrated, that T_c is essentially a property of *a single-unit-cell thick layer* of Bi-2212 (or Bi-2223), it is clear that one needs to interpret the reported *R(T)* curves with great caution. An important indicator is the surface roughness of such a film; in the best cases, we have seen rms roughness as small as 1-2 Å, and in such case one would not expect massive intergrowth defects. A typical AFM image of the LSCO films surface grown in our ALL-MBE system is shown in Figure 5a. The RHEED image recorded at the end of the film growth is presented in Figure 5b; the intense specular spot indicates atomically flat surface.

Here, we wish to emphasize that we have given above just two examples of atomic-layer engineering that we were involved with. Several other groups, and in particular

those led by J. Eckstein, M. Naito, T. Kawai, H. Koinuma, G. Balestrino, etc., have accomplished impressive results with other compounds and synthesized various superlattices and "artificial' superconducting materials, e.g., by employing epitaxial stabilization. However, it is definitely out of the scope of the present brief report to review extensively the results of this entire field, for which we apologize.

IV. COMBE

Our MBE system has another unusual characteristic: the metal atom sources are aimed at the substrate at a steep angle of about 20^0 (see Fig. 2). This renders a large composition spread (gradient) in radial direction along the source flux (and the substrate array). At the same time the composition spread in transverse direction over the sample area is very small, essentially negligible. This allows one to synthesize combinatorial sample libraries – a single film with a large but known and position-addressable spread in chemical composition. [8]

For greatest flexibility, we use pairs of identical sources placed in opposite azimuth positions, i.e., with the atomic beam impinging at the same angle with respect to the substrate(s), but from the opposite sides. This arrangement enables us to control the gradient of the corresponding atomic flux along the substrate over a wide range. The maximum gradient is obtained when one source is open and its counterpart is closed. The minimal gradient, close to zero, is achieved when both sources are open and emit the same atomic fluxes. Any intermediate value of the gradient can be obtained by adjusting the deposition rates from opposite sources of the same element. This can be accomplished e.g., by adjusting the temperature of each of these two sources and/or by adjusting the time intervals during which the source shutters are kept open. To measure the deposition-rate gradient across the substrate array, we use a quartz-crystal rate monitor (QCM) mounted on a motorized, computer-controlled, three-degrees-of-freedom manipulator. In this way, we have verified that the profile of the rate of deposition from a single atomic source in our COMBE system is essentially linear.

To make a good use of combinatorial synthesis, one also needs a high-throughput sample characterization. Apart from using AFM and scanning XRD, we also built and used a multiple-probe (64 channel) set-up for measuring the spread in resistance within

each substrate as a function of temperature down to $T = 4.2$ K. This set-up allowed us to measure $R(T)$ characteristics of all the 64 pixels simultaneously. We are recently completed construction of a 32-channel Hall voltage measurement setup as well.

In the present context of search for novel superconductors with ever-increasing T_c, our combinatorial synthesis and characterization capabilities may be useful insofar that they allow one to quickly find the chemical composition corresponding to the highest T_c within a given solid-solution range. In combination with our unique surface-analysis tools and atomic engineering capability, this makes us well equipped for the task at hand.

V. The future: prospects and challenges

Building on the present expertise, we will keep trying to further develop the ALL-MBE synthesis technique. We hope to further improve film quality and expand the study to include other complex oxides, and plan to try synthesis of other novel metastable compounds and superlattices. Improvement in film quality and synthesis of different superlattices may provide new insights in the physics of strongly correlated oxides. With improved understanding, and hopefully with some useful input from theorists, our chances to actually discover novel and better superconductors should increase.

However, one should recognize that the task is not simple. Nature herself imposes some constraints.

The first problem is mixing of atoms from different layers. In order to achieve good crystallinity, we like to deposit films at a high temperature, close to the melting point if possible. However to make superlattices with sharp interfaces the bulk mobility of the atoms should be small, or else there will be much interdiffusion. So the challenge is to find a certain window in thermodynamic parameters (temperature, pressure) where the bulk mobility is low enough so that the layers do not mix, and yet the surface mobility is still large enough to enable atoms to order into a highly crystalline structure. In this regime, one may be able to influence the film synthesis by controlling the sequence in which atoms are supplied to the growing film surface.

The second issue is that MBE growth process starts from the substrate surface, and it depends strongly on whether the interface between the substrate and the epitaxial overgrowth is crystallographically perfect or not. The most frequent case in MBE growth is

hetero-epitaxy, namely, epitaxial growth of a layer with the chemical composition and structural parameters different from those of the substrate. As an example, for substrate we frequently use $LaSrAlO_4$ (LSAO) and $SrTiO_3$ (STO). The crystal lattice constant in STO is $a = 3.905$ Å, which is 3 % larger than the in-plane lattice constant of bulk LSCO, $a = 3.777$ Å for optimal doping (x = 0.15). Hence, LSCO films are under tensile strain on STO substrates. In contrast, LSAO has a 0.5 % shorter lattice constant, $a = 3.755$ Å, and on such a substrate LSCO film is under compressive strain. This difference in epitaxial strain allows one to manipulate the transport properties and T_c. Several groups [11,12] observed T_c enhancement in thin epitaxial LSCO films on LSAO substrates (i.e., under compressive strain) as compared with similar films on STO substrates. However, we have found that the main mechanism of the T_c enhancement in this case was the shift in oxygen doping level; epitaxial strain assists oxygen incorporation into the lattice [13]. This illustrates the need to understand and hopefully utilize the crystallographic strain.

The next problem to consider is the difference in electronic properties of different oxides layers; this may cause carrier depletion and accumulation, and electron-band banding. Electronic properties of layers near the interfaces may be modified on the length scale of several unit cells. This makes the physics of superlattices somewhat obscure, because in general we do not know upfront the modified electron band structure. On the bright side, this electron-band banding can be utilized, in principle at least, in synthesis of new materials with properties that are unusual and very different from those of the bulk constituents.

Complex oxides exhibit an enormous range of properties, and holed many records - they are the strongest dielectrics, ferroelectrics, ferromagnets, and last but not least, the strongest known superconductors with the highest T_c above 160 K. Hence, the range of possible combinations is very large. Thus we need some luck and/or theoretical guidance here: which pairs to try (first). One possible choice is for one constituent to be a metal and the other to be an insulator, as in the Ginzburg quasi-2D excitonic superconductor. There may be others – we are open to suggestions.

ALE MBE enables material engineering at various levels. By stacking of molecular layers of different compounds, one can form multilayers and superlatices of different compounds. Within a molecular layer, one can add or omit atomic monolayers. It is even

possible to modify individual atomic layers, e.g. by doping. We could also engineer strain, electron accumulation and depletion, and band bending. In this way, we can cast novel compounds – perhaps with interesting physical properties, among which a high T_c would be highly desirable. While it may be difficult to know exactly where to look, we may leverage on our COMBE capability to synthesize and test hundreds of compositions at once.

In conclusion, it seems worth trying to search for high-temperature superconductivity in artificially layered oxides: first, because high-T_c superconductivity was discovered in layered cuprates; second, because Ginzburg and Bardeen said as much – and they have been right before; and third, because we can - we now have a technique to do it.

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Dielectric
Metal
Dielectric
Metal
Dielectric
Metal

- $(LaSr)_2O_2$ -
- CuO_2 -
- $(LaSr)_2O_2$ -
- CuO_2 -
- $(LaSr)_2O_2$ -
- CuO_2 -

(a)   (b)

Figure 1:   (a) Ginzburg's excitonic superconductor

(b) Layered structure of the high-T_c superconductor $La_{2-x}Sr_xCuO_4$.
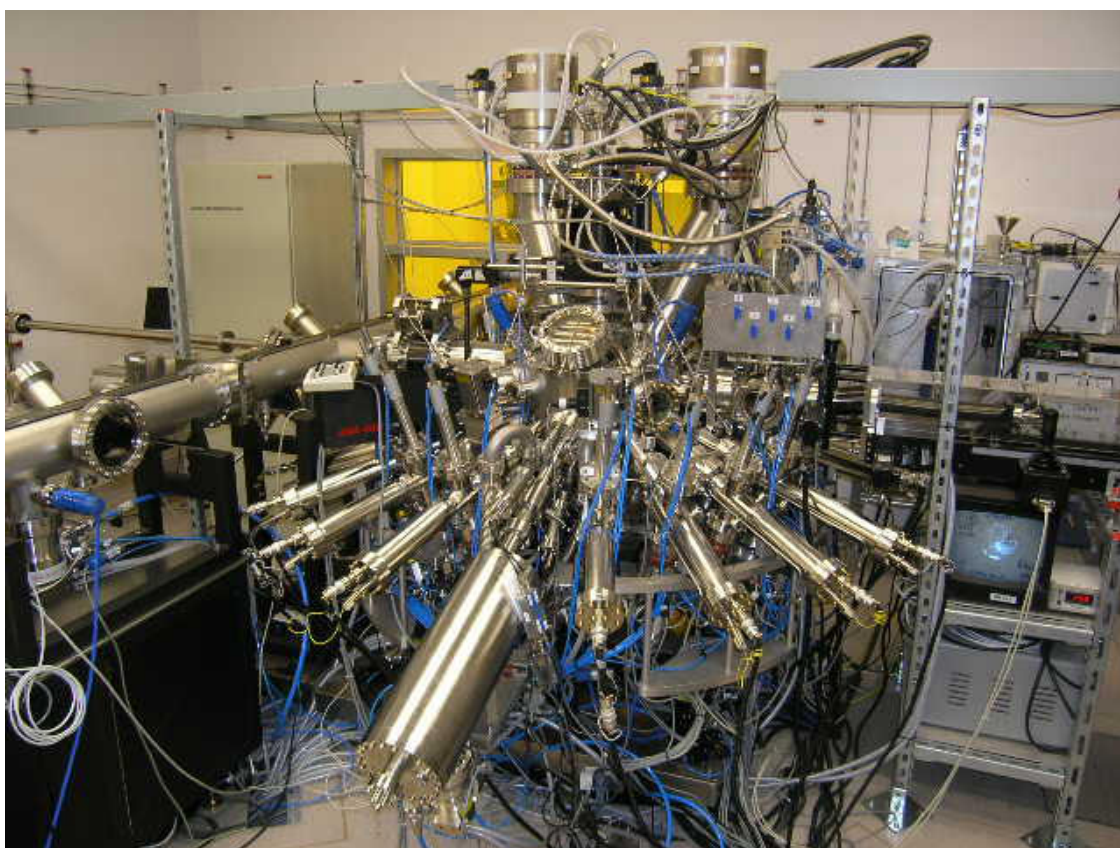
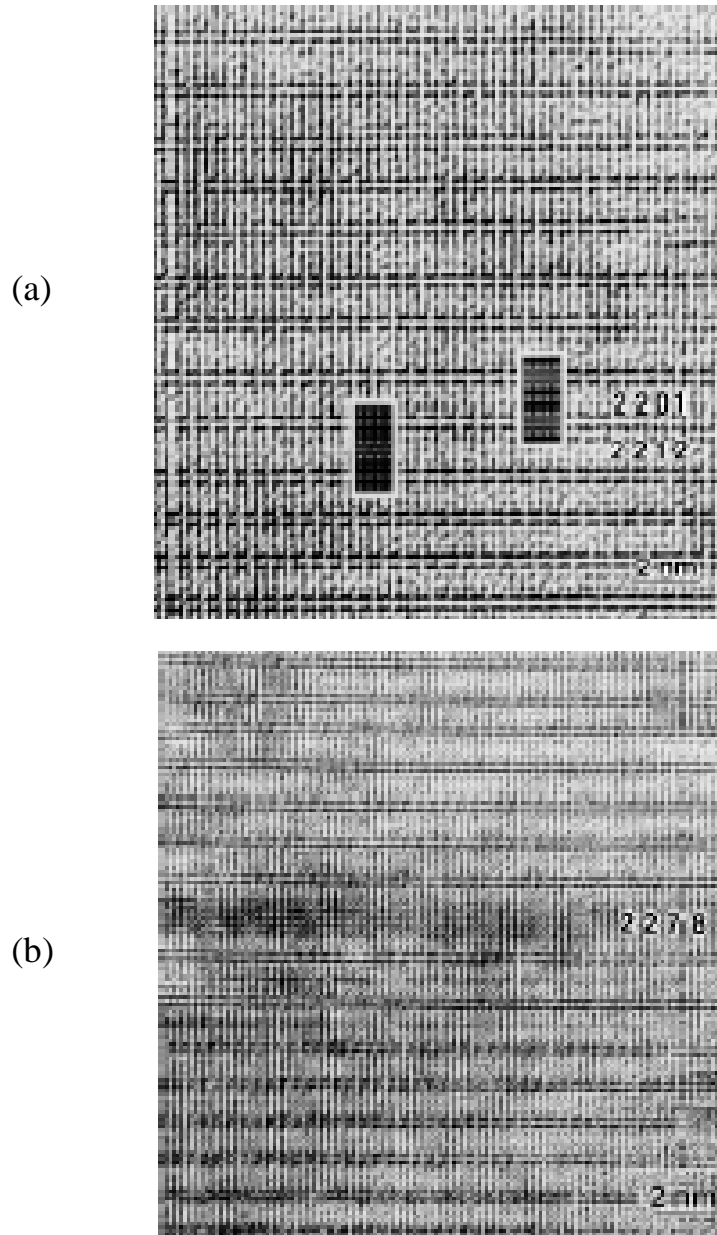Figure 2:   The ALL-MBE system at Brookhaven National Laboratory.

Figure 3:   (a) A high-resolution cross-section TEM image of a Bi-2201 / Bi-2212 superlattice. The view is along the (001) axis of an STO substrate. The alternation of the 15.4 Å lattice period of Bi-2212 and 12.3 Å period of Bi-2201 is readily identifiable.

(b) A cross-section image of a Bi-2278 barrier layer sandwiched between two thick layers of Bi-2212. (After Ref. [10]).
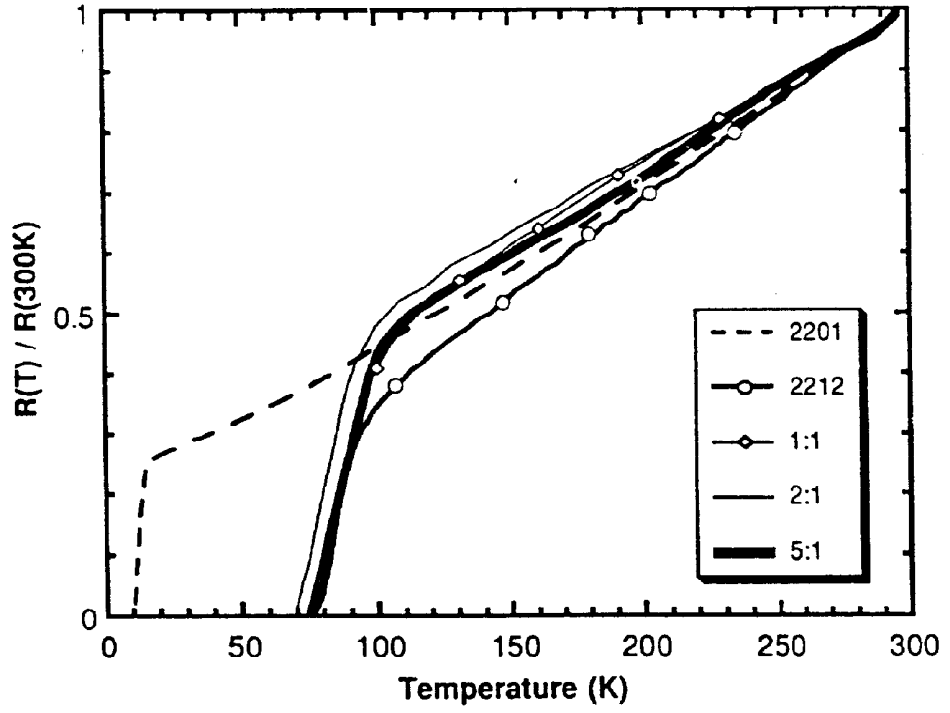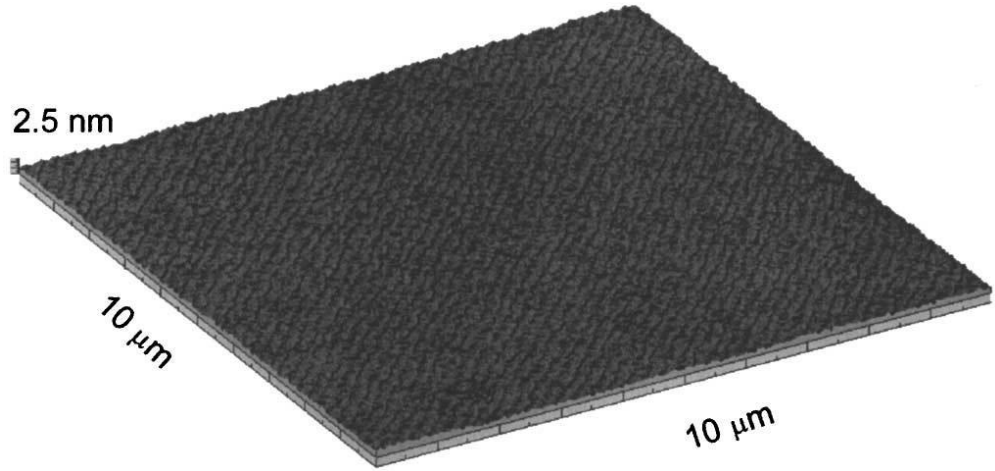
Figure 4. Normalized resistance vs. temperature for (a) single-phase Bi-2201 film, (b) Bi-2212 film, (c) Bi-2212 : Bi-2201 superlattice, (d) Bi-2212 : (2×Bi-2201) superlattice, and (e) 2212:(5× Bi-2201) superlattice. The films were grown by ALL-MBE [2].

(a)

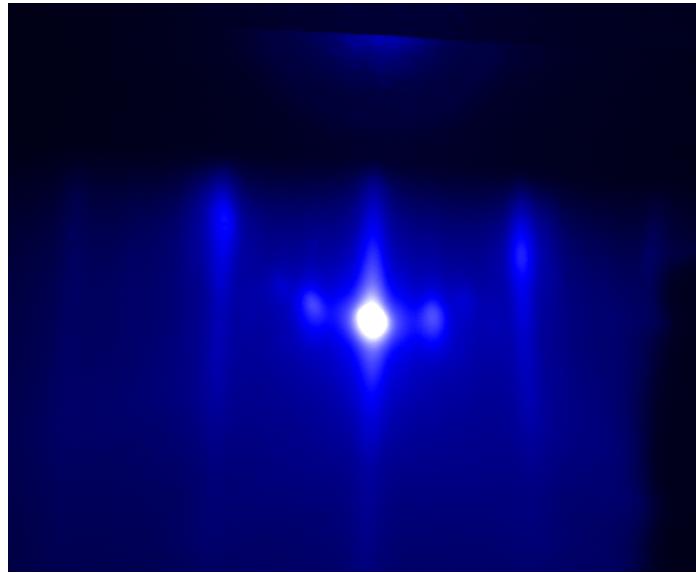
2.5 nm

10 µm

10 µm

(b)

Figure 5:   (a) A 3D AFM image of a 78 nm thick LSCO film on LSAO substrate. It shows terraces, about 300 nm wide, between one unit cell tall steps, as a consequence of a slight (0.1°) miscut of the LSAO substrate. The rms surface roughness of this film was 3 Å over the area of 2500 μm^2. (After Ref [14]).

(b) A RHEED image at the end of the epitaxial LSCO film growth.